Chemical Weathering and Mineralogy of McMurdo Dry Valley Streams: Examining the Controls of Current and Future Ephemeral Stream Geochemistry

Research Thesis

Presented in partial fulfillment of the requirements for graduation with research distinction in Geological Sciences in the undergraduate colleges of The Ohio State University

by

Jordan Scheuermann

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Project Advisor: Professor W. Berry Lyons, School of Earth Sciences

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Abstract. The McMurdo Dry Valleys form the largest ice-free region in Antarctica and are the coldest, driest deserts in the world. But, for approximately 6-12 weeks per year in the austral summer, continuous sunlight and near-freezing temperatures create meltwater streams that descend from the surrounding alpine glaciers. These ephemeral streams are a distinctive feature in the barren dry valley landscape and are important sources of nutrients and solutes from the weathering of streambed and hyporheic zone materials. This setting has been a US National Science Foundation funded Long-Term Ecological Research (LTER) project since 1993. A major goal of the McMurdo LTER is to understand how liquid water, the primary limiting condition for life in Antarctica, is affected by climate variability. The McMurdo Dry Valleys are extremely climate-sensitive and even seemingly small variations in temperature can have a drastic effect on hydrological activity. The McMurdo LTER program has been successful in collecting and analyzing a large amount of stream data pertaining to weathering products but, a more comprehensive analysis and interpretation of the data have yet to be undertaken. Assessment of current and future stream geochemistry is critical to predict the impact of increased water flow due to glacier melt and increasing temperature which could greatly influence the ecological function and biologic diversity in the McMurdo Dry Valleys. Surface sediments were collected at multiple locations from ephemeral streams and analyzed using a scanning electron microscope and x-ray diffraction to determine sediment mineralogy and evidence of chemical weathering. Geochemical reactions were modeled using previously collected stream water data and the USGS PHREEQC software for the speciation calculations and the assessment of the solubility controlling solid phases. Chemical weathering was apparent through visible mineral alteration and the formation of secondary weathering products. Modeling results indicate that stream geochemistry will not significantly be affected by increased water temperature in the future. These results suggest stream geochemistry and chemical weathering may instead be controlled primarily through hydrologic exchange in the hyporheic zone.

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1. Introduction. Chemical weathering is an important surficial process that produces soils, shapes the landscape, provides nutrients to plants, neutralizes natural and anthropomorphic acidic precipitation, and provides solutes to streams (Nezat et al., 2001). Over long periods of geologic time, the chemical weathering of silicate minerals also affects global climate by consuming carbon dioxide, a major greenhouse gas. Atmospheric carbon dioxide dissolves in water to form carbonic acid. During chemical weathering the carbonic acid reacts with silicate minerals to produce bicarbonate which is then removed from the water in the form of carbonate precipitation or organic matter deposition. As carbonic acid is the only source of the bicarbonate ions in the reaction, silicate weathering creates a net loss of CO_2 from the atmosphere. Work in temperate regions has led to the assumption that climate is the primary control of chemical weathering, in particular temperature and precipitation. The relationship between chemical weathering and climate is that the higher temperature and/or precipitations, the higher rates of chemical weathering. Previous studies in the McMurdo Dry Valleys have demonstrated that chemical weathering in polar environments does not follow historical chemical weathering assumptions, in that even at the average mean temperatures of these environments, rapid chemical weathering does occur (Green et al., 1988; Nezat et al., 2001; Maurice et al., 2002).

Numerous experiments have demonstrated that chemical weathering is occurring in McMurdo Dry Valley ephemeral streams (Green et al., 1988; Lyons et al., 1997; Welch et al., 2010). Dry Valley stream geochemistry is controlled by the hydrologic exchange and the chemical weathering of primary allumiosilicate minerals within the hyporheic zone as represented by the equation:

(1) Primary aluminosilicate + CO_2 + H_2O → weathering product +HCO_3^- + dissolved cation + H_4SiO_4

Chemical denudation rates of H_4SiO_4 calculated in Taylor Valley streams are the same order of magnitude as the world average ($64 \cdot 10^3$ moles$\cdot km^{-2} \cdot yr^-$) and suggest that chemical weathering is occurring (Nezat et al., 2001; Gooseff at al., 2002). Nezat et al. (2001) demonstrated that chemical denudation rates increase and decrease with corresponding changes in discharge from year to year and between streams in Taylor Valley during a single austral summer. The flux of meltwater in the hyporheic zone is directly related to stream discharge. The input of dilute water to the hyporheic zone dissolves weathering products from the mineral surfaces, thereby producing fresh mineral surfaces and increasing dissolution (Gooseff et al., 2002). Therefore, an

increase in stream discharge will result in an increase of chemical weathering. Maurice et al. (2002) provided a direct observation of dissolution features on mica chips buried in hyporheic zone sediment. The dissolution features are small, shallow, anhedral etch pits and are evidence of rapid initial dissolution rates at the beginning of the austral summer. Their occurrence suggests chemical weathering can occur during the short period of time meltwater flow is available. These findings indicate that other factors may be significantly affecting chemical denudation rates in polar deserts. For example, high rates of physical weathering, which continually expose new, largely unweathered rock surfaces to relatively dilute glacial meltwater play a significant role. Stream morphology is another factor that has been shown to affect chemical weathering rates. Low-gradient streams tend to have a larger hyporheic zone, especially during high flow, which increases the ratio of water to sediments surfaces thus increasing chemical weathering (Nezat et al., 2001). The establishment of the MCM-LTER has made extensive long term studies of stream geochemistry possible. For example, Welch et al. (2010) suggested a geochemical gradient between Taylor Valley streams is a function of position within Taylor Valley which includes factors such as the distance to the ocean, lithology of surface sediments, age of the till sheets, and past climatic history (Barrett et al., 2006).

This study explored the controls of chemical weathering in an extreme polar environment. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were utilized to characterize the weathering products found in ephemeral stream surface sediment. Minerals identified during SEM analysis were used to constrain possible XRD results. The SEM analysis offered a direct observation of possible secondary weathering products and dissolution of primary aluminosiliacte minerals. Previous work has often failed to offer direct evidence of predicted geochemical results. XRD results were utilized to compile a comprehensive mineral list of Dry Valley streambed sediments that may be influencing stream geochemistry. The geochemical software, PHREEQC, was used to model the saturation index of select minerals found during SEM and XRD analysis using MCM-LTER stream chemistry data beginning in the 1994/95 field season. The long-term trends in saturation indices provided insight into past stream geochemistry and chemical weathering trends and controls. Finally, the function of temperature in chemical weathering in polar climates was examined by modeling mineral solubility under increased temperature conditions.

2. Field Description.

2.1 McMurdo Dry Valleys. The McMurdo Dry Valleys (76°30′-78°00′S, 160°00′-165°00′E) in southern Victoria Land, Antarctica are the largest ice-free region on the continent and encompass 4500 km^2 of ice-free terrain (Levy, 2013). The McMurdo Dry Valleys are defined by the Transantarctic Mountains, which block the ice flow of the East Antarctic Ice Sheet (EAIS), to the west and the McMurdo Sound to the east. The McMurdo Dry Valleys are considered a polar desert and the extreme environment that is dominated by soils derived from glacial tills, ephemeral steams, emanating from the surrounding alpine glaciers, and more than 20 permanent lakes and ponds (Fountain et al., 1999). Ventifacts, rocks that have been sculpted by wind-driven sand, are common and provide evidence of the consistently high winds and arid nature of the Dry Valleys. For nearly four months of the austral summer continuous daylight occurs and surface temperatures range between -10 and 5°C. Winter is blanketed by endless darkness with temperatures falling between -40 to -8°C (Doran et al., 2002).

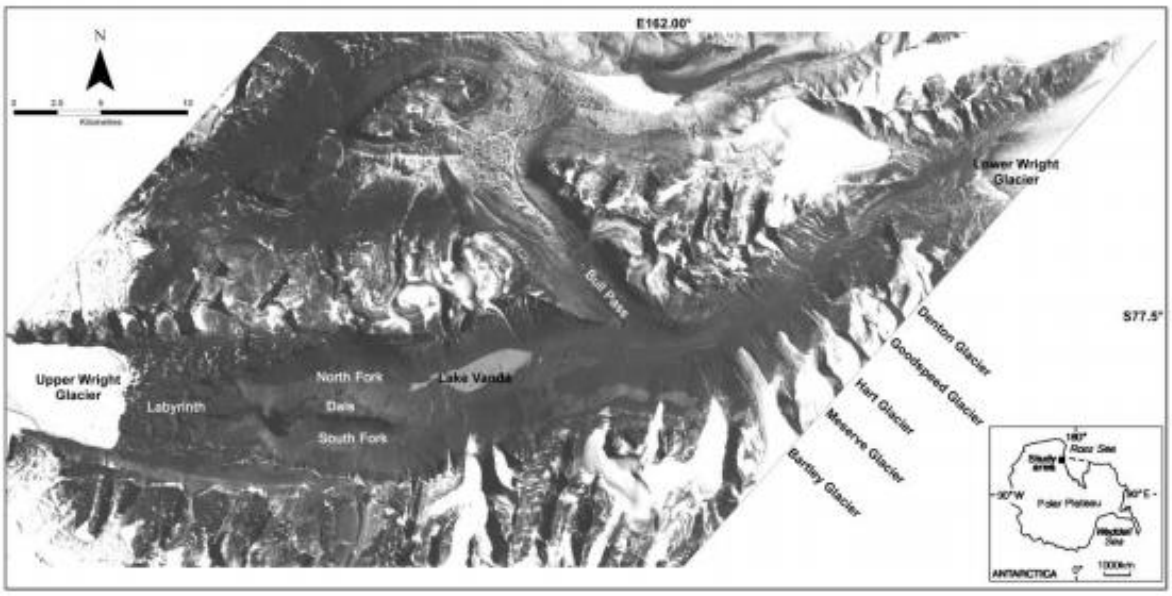

Figure 1. Map of Wright Valley, Antarctica (adapted from McLeod, 2012)

2.2 Wright Valley. Wright Valley (77°32′S, 161°34′E) is the central of the three largest Dry Valleys positioned between Victoria Valley and Taylor Valley (Figure 1). Wright Valley cuts inland over 80 km from the McMurdo Sound to the ice cap of the Polar Plateau. It measures approximately 10 kilometers at its widest point from the Olympus Range to the north and to Asgard Range to south. At the mouth of the valley, the Wright Lower Glacier separates Wright

Valley from the McMurdo Sound and the Ross Sea. The Onyx River, the longest river in Antarctica, flows from the Lower Wright Glacier to Lake Vanda, which is almost 30 km inland.

2.3 Taylor Valley. Taylor Valley (77°40′S, 162°52′E) is south of Wright Valley between the Asgard Range to the north and the Kukri Hills to the south. Taylor Valley extends approximately 33 km from the Polar Plateau to the Ross Sea and measures 12 km wide (Figure 2). A climatic gradient exists in Taylor Valley- the western portion of the valley is warmer, drier, and windier than the valley adjacent to McMurdo Sound. This is partly due to the katabatic winds that warm adiabatically while they descend from the Polar Plateau (Fountain et al., 1999). The Nussbaum Rigel, located about 20 km inland, trends north-south across Taylor valley and augments the climatic differences in the Valley by confining the katabatic winds and preventing the precipitation-laden storms from reaching Lake Bonney. Taylor Valley has abundant streams that flow into three closed-basin lakes, Bonney, Fryxell, and Hoare.

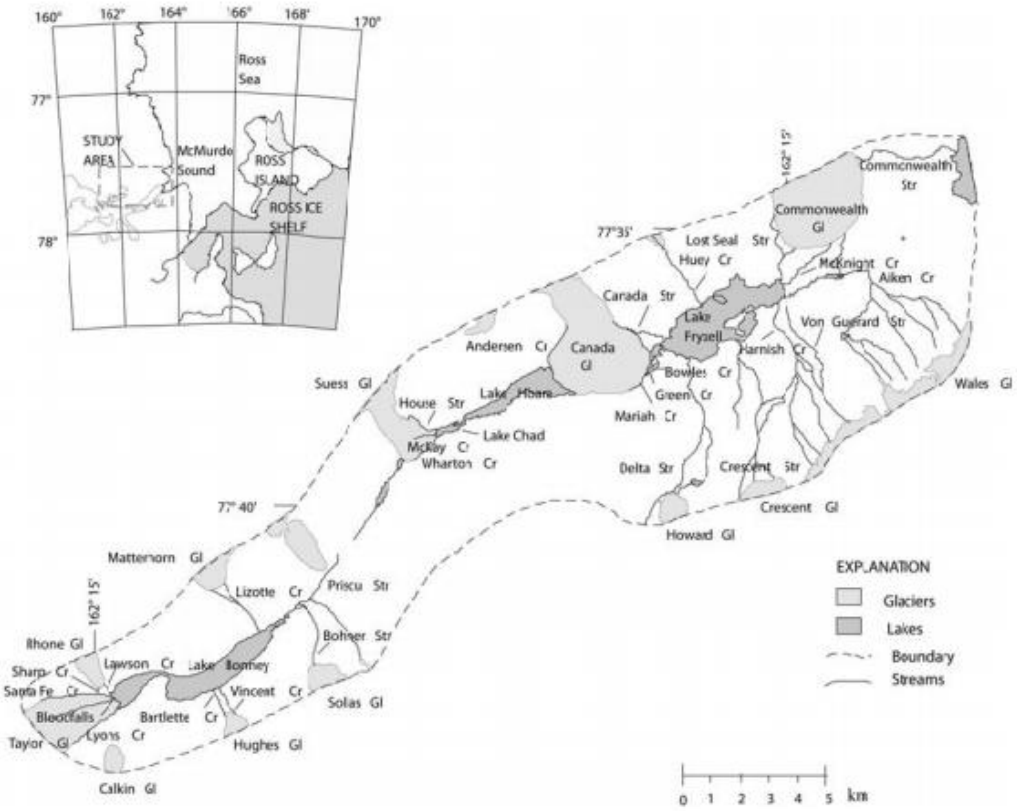

Figure 2. Map of Taylor Valley, Antarctica (adapted from Welch et al., 2010)

2.4 Geology. The basement geology of the McMurdo Dry Valleys includes pre-Ordovician schist, hornfels, and marble metasediments; Paleozoic granite; and amprophye and granitic

dykes. It is overlain by the Beacon sandstone. The Jurassic-age Ferrar dolerite sills cut through both the basement rocks and Beacon Supergroup (Maurice et al., 2002). Sedimentary, igneous, and metamorphic rocks can be found in the McMurdo Dry Valleys. Large portions of the valley floors are covered by desert pavement of mostly sand sized particles interbedded with cobble and boulder sized rocks primarily composed of granite, marble, gneiss, dolerite and sandstone (Doran et al., 1994). Deltaic deposits of silt and clay carbonates from older proglacial lakes are also common within Taylor Valley. Numerous advances and retreats of the East and West Antarctic Ice Sheets create the till on the valley floors. The EAIS moves west to east down Taylor Valley during interglacial times towards the McMurdo Sound. The West Antarctic Ice Sheet moves north along the Victoria Land Coast during glacial times and spills into eastern Taylor Valley. Hence, the till deposits found from the McMurdo sound coast into the Fryxell basin, the Ross Sea Drift, are much younger than the interglacial deposits in the Hoare and Bonney basins, the Bonney drift (Barret et al., 2006). Kenyte, a rare phonolite which outcrops on Ross Island but not in Taylor Valley, is found in the eastern half of Taylor Valley. Therefore, its extent in Taylor Valley marks the furthest advance of the WAIS. The Ross Sea Drift is largely composed of diorite and granite although kenyte, Ferrar Dolerite, and McMurdo Volcanic Group rocks are also present. In comparison, the Bonney Drift is dominated by granodiorite/granite-gneiss/diorite with less Ferrar Dolerite and marble than the Ross Sea drift (Barret et al., 2006).

2.5 Glaciers. Three types of glaciers are found in the McMurdo Dry Valleys: alpine glaciers descending from the surrounding mountains, piedmont glaciers along the coast, and outlet glaciers from the East Antarctic Ice Sheet (EAIS). Fifteen polar alpine glaciers descend from the Asgard Range and the Kukri Hills in Taylor Valley with the largest glaciers reaching the valley floor and terminating in steep cliffs up to 20 m high. Glaciers are a central feature in Taylor Valley and cover almost 40% of the surface area (Lyons et al., 2003). Unlike temperate glaciers, the net mass gain and loss of polar McMurdo Dry Valley glaciers is small, in contrast to the global trend of retreating alpine glaciers. About 70% of Dry Valley glacier mass loss is due to sublimation with the remainder due to melt during the austral summer (Fountain et al., 1999). Runoff is limited to surface or near-surface flow and often flows from the cliffs at the termini. Internal temperatures of the ice are well below freezing and the glaciers are frozen to the substrate. Topographic differences cause the glaciers flowing from the Asgard Range to be approximately three times larger than the glaciers originating from the Kukri Hills. This is a

consequence of the north facing Kukri Hills, which receive more radiation than the Asgard Range, in addition to the larger accumulation basins found in the Asgard Range (Fountain et al., 1999). Taylor Glacier, an outlet glacier of the Polar Plateau, is the largest in Taylor Valley. In Wright Valley, Upper Wright Glacier is an outlet glacier from the EAIS, but is considerably smaller than Taylor Glacier. In the eastern region of the valley the piedmont glacier, Wright Lower Glacier, flows very slowly westward up valley.

2.6 Ephemeral streams. Meltwater generated from the ablation zone of the surrounding alpine glaciers is the principal source of water to Taylor Valley streams and link the glaciers to the perennially ice covered closed-basin lakes on the valley floor (Fountain et al., 1999). Streams are hydrologically isolated, do not receive overland flow, and do not have groundwater input (Chinn, 1993). As snow falls it quickly sublimates (Chinn, 1981). Snowfall occurs anytime of the year, but does not play a meaningful role as a contributor of water to Dry Valley streams. Ephemeral streams can flow from late November to early January, ranging from 4 to 10 weeks, in well-defined, stable stream channels that range in length from less than 1 km to over 24 km (Gooseff et al., 2011). Taylor Valley glacial meltwater streams are mostly first order, less than 30 cm deep, and typically range from 1 to 10 m in width (Green et al., 1988). Temperatures generally hover around 0°C and even seemingly small temperature variations can cause fluctuations in discharge. Moreover, solar radiation throughout McMurdo Dry Valleys is variable resulting in intermittent streamflow on all temporal scales. Stream flow has been observed to vary by as much as 5 to 10 fold in a single day (Conovitz et al., 1998). In total, 27 ephemeral streams are located in Taylor Valley, all of which flow through unconsolidated alluvium. Although, there is a spatial difference in general stream gradient between the shallower streams in the east to the steeper Hoare and Bonney Basins to the west (Nezat et al., 2001).

Small by temperate standards, the Onyx River, situated in Wright Valley, is the longest stream in Antarctic at more than 30 km long and measures 50 cm in depth and 10 m in width. Unlike most Taylor Valley streams, the Onyx River flows up valley westward from the Wright Lower Glacier and Lake Brownworth through bedrock channels, alluvial flats, moraine, and boulder pavement into Lake Vanda, a highly stratified, closed basin lake (Green et al., 2005). Permafrost is continuous throughout the McMurdo Dry Valleys at shallow depths (average active layer is about 50 cm thick) and confines groundwater flow to a near surface hyporheic zone (Figure 3) that can be easily discerned as a damp band of sediment adjacent to the stream channel (Campbell at al., 1998; McKnight et al., 1999). This thawed soil neighboring and underneath the stream channel is highly permeable alluvium, known as the "hyporheic zone", allows for rapid exchange rates of water with the main channel. This zone becomes saturated before water can flow downstream (Gooseff et al., 2011). The primary control of the depth of the hyporheic zone is the extent of the active permafrost layer. At the beginning of the austral summer, the active-layer thaw depth of Taylor Valley streams was 5 to 10 cm, but grew to 50 to 60 cm by the end of the summer (Conovitz, 1999).

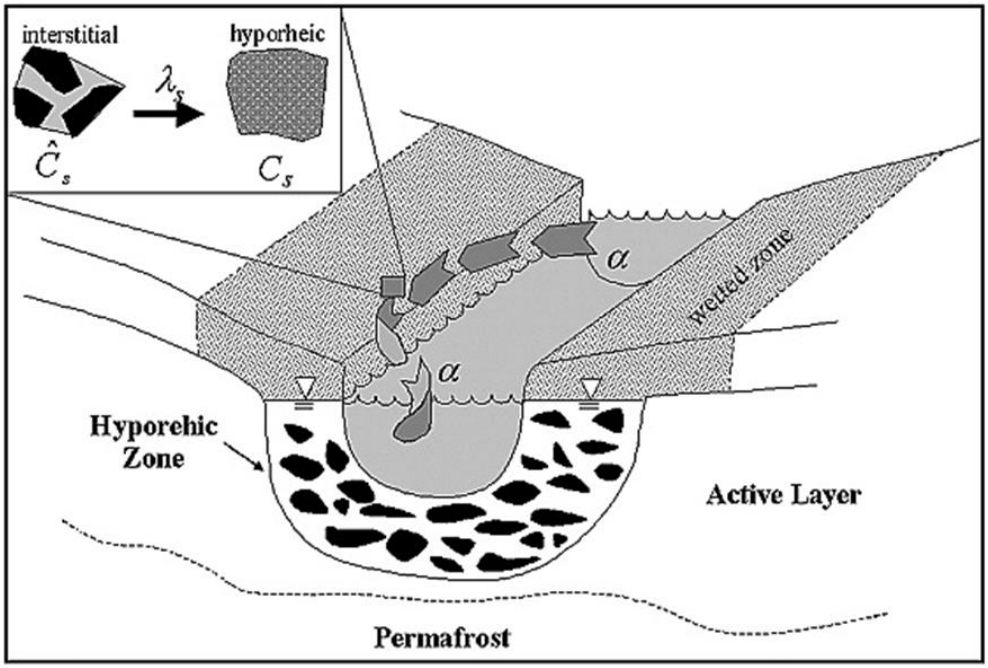

Figure 3. Cross section of the hyporheic zone found in Antarctic streams. (adapted from Gooseff et al., 2002)

2.7 Lakes. Most of the lakes in the McMurdo Dry Valleys are highly stratified, saline, closed-basin, and perennially covered with 3 to 6 m of ice (Fountain et al., 1999). Lake Bonney, Lake Hoare, and Lake Fryxell are the three major lakes in Taylor Valley. Lake Bonney is the westernmost Taylor Valley lake and is 7 km long and 900 m wide. It is separated into two distinct lobes by a narrow channel approximately 50 m wide. Lake Hoare is just over 4 km long and 2 km wide and is dammed by Canada Glacier. The easternmost Taylor Valley lake, Lake Fryxell, sits between Canada and Commonwealth glaciers (Figure 2). The largest lake in Taylor valley by surface area, it measures 6 km long and 2 km in width. Lake Vanda, measuring over 5 km long and a depth of about 70 m, is the largest lake in Wright Valley (Figure 1). The most important feature of Dry Valley lakes is their perennial ice cover that distinguishes Dry Valley from any other lakes on the planet. The thick ice cover acts as a buffer from the extreme Antarctic environment and isolates the water from atmospheric effects, like mechanical mixing by wind (Doran et al., 1994). Hydrologic input to the lakes is limited to ephemeral stream flow in the austral summer. Most lakes develop a moat during the summer months that allows stream flow to reach underneath the ice (Gooseff et al., 2011).

3. Methods.

3.1 Chemical Analysis. As part of the McMurdo Dry Valleys Long-Term Ecological Research (MCM-LTER) Program, streams have been sampled during the austral summer from 1993 to present. On a weekly basis most streams are sampled just upstream from the stream gauge. However, due to the intermittent nature of the stream flow, sampling does not always follow a consistent schedule. Water samples are filtered using Nucleopore polycarbonate membrane filters with a 0.4 µm pore size. Cation samples (Li^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) are filtered into HDPE bottles that have been rinsed with 1% or 10% HCL solution and subsequently rinsed five times with ultra-pure water. Ultrex nitric acid is added to preserve the samples to a pH of ~2-3. Anion (F^-, Cl^-, and SO_4^{2-}) and H_4SiO_4 samples are filtered into HDPE bottles that had been rinsed five times with ultra-pure water. Samples are then stored at approximately 4ºC until analysis. Major ion analyses were determined at Crary Laboratory at McMurdo Station using a Dionex DX-120 using methods that have been described in detail by Welch et al. (2010). Temperature and pH were measured using calibrated probes soon after sampling. Alkalinity (i.e. HCO_3^-) and dissolved silica (H_4SiO_4) samples are shipped back to Ohio State and analyzed using acid filtration and colormetric techniques described in detail in Welch et al. (2010).

3.2 Surface Sediment Analysis. Ephemeral stream surface sediments were collected throughout Taylor Valley during the 2002/2003 field season. Samples were collected with a polyethylene scoop, stored frozen in plastic bags, and then dried at the Byrd Polar Research Center at The Ohio State University. Sand and gravel sized particles were examined using a FEI Quanta 250 Scanning Electron Microscope (SEM) equipped with a Bruker energy dispersive X-ray spectrometer (EDS). Small sand to granule sized sediment samples were placed upon an aluminum stub using doubled sided carbon tape and subsequently coated with a palladium/platinum spray to prevent charging in the SEM. Grain mineralogy was determined comparing the relative intensity of element X-ray signals from the EDS detector, grey scale level from the back scattered electron detector, and grain morphology. Further mineralogical analysis was determined by X-ray diffraction (XRD). Stream sediment samples were crushed using a ceramic mortar and pestle until the samples were a fine powder. The sediment was loaded into a stainless steel holder using a randomly orientated pressed powder. XRD analysis utilizes the unique crystal structure inherent to a specific mineral to identify all minerals present in the

powder. The diffraction of X-ray though each mineral's crystalline structure produced a unique diffraction pattern. Grain mineralogy was identified by peak profile fitting using the search-match algorithm feature of PANalytical HighScore Plus. An example of the graphical output of the PANalytical HighScore Plus software is shown in Figure 4.

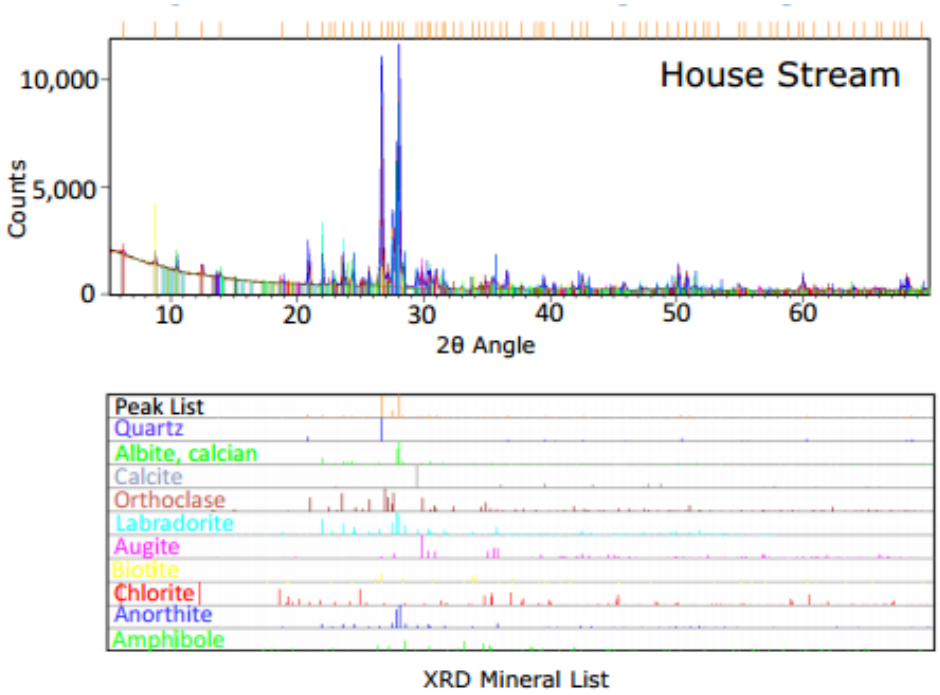

Figure 4. House Stream XRD results. Minerals peaks with their corresponding 2θ angle (top) and the complete list of minerals found in the XRD analysis (bottom).

3.3 PHREEQ. PHREEQC, which is an acronym for pH, redox, equilibrium, and the computer program it is written in, C, is an aqueous geochemical modeling program. Geochemical modeling using PHREEQC was conducted utilizing measured major solute concentrations from the Taylor Valley streams and the Onyx River in order to determine speciation and saturation state indices for expected primary and secondary mineral phases present in batch sample solution using methods of Parkhurst and Appelo (2013). The saturation index, SI or Ω, is defined by the equation: $SI=\log(\frac{IAP}{Ksp})$. Where the solubility product, or K_{sp}, is the equilibrium constant for a solid or precipitate substance in an aqueous solution and represents how readily a substance will dissolve in the solution of the specific chemistry of a solution. The more soluble a substance is, the higher K_{sp} it will have. The solubility product is the product of the concentrations of the ions

in solution, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium The ion activity product, IAP, is the concentration of the dissolved solutes that make up a "salt" in a given stream sample that has been corrected to activities to account for ion-ion interactions within a solution. If IAP > K_{sp}, the solution is supersaturated in respect to a given mineral and the saturation index is positive. In this case, deposition of the mineral would occur. If IAP = K_{sp}, the solution is in equilibrium, or saturated, and the saturation index would be equal to zero. If IAP < K_{sp}, the solution is undersaturated with respect to a given mineral and the saturation index would be negative. Over time, the mineral will dissolve in solution. PHREEQC was also utilized to calculate the solubility "fate" of the possible mineral phases given the ion, water temperature, pH, and alkalinity data collected from MCM-LTER.

In addition to the measured major ions, an aluminum concentration of 1 μg/L was used in all PHREEQC calculations and Br^- concentrations were used when measured. For each field season, the ion concentration and field measurements from the third week of January were used. If no ion concentrations or field measurements were recorded during this time, the data taken closest to the time was used.

The 2009/10 field season temperature data were used to model the saturation index under increasingly higher temperatures in an attempt to predict changes in stream geochemistry in the face of future global climate change. The saturation index of select minerals in the Taylor Valley streams of Anderson Creek, House Stream, and Lost Seal Stream was modeled at 5°C, 10°C, and 20°C. A temperature of 5°C is in the range of temperatures recorded during the study period, but represents an elevated baseline for the majority of recorded water temperatures. A temperature of 10°C is close to the maximum recorded water temperature and provides a plausible uniform water temperature under future climate conditions. A temperature of 20°C is an extreme case and comparable to temperate streams conditions. All ion concentrations and pH data remained unchanged so that water temperature was the sole variable.

4. Results.

Since the establishment of the MCM-LTER Program in 1993, stream data have been collected every austral summer. In this thesis, 12 seasons of data are examined from the 1994/95 field season to the 2010/11 field season for five streams in Taylor and Wright Valley. The four Taylor Valley streams are Anderson Creek, House Stream, Lost Seal Stream, and Priscu Stream. In Wright Valley, the Onyx River is studied. These streams were chosen to reflect the different types of streams present in the Valleys. The absence of field measurements like temperature and pH data was largely the cause for an omission of a season's data as they are critical to accurate saturation index calculations. Streams are sampled on a weekly basis, but the unpredictable nature of stream flow does not always allow for sampling to follow a strict schedule.

4.1 Chemical Analysis. Anderson Creek and House Stream are south facing streams and had the least variation of water temperature with less than 3°C of difference between the minimum and maximum observed temperatures. These streams also were the coldest. A maximum water temperature of 2.9 °C was recorded in Anderson Creek during the 2007/08 season and a maximum of 2.2°C was recorded in House Stream during the 2006/07 field season. The warmest recorded temperature in Priscu Stream was 11.2°C during the 2002/03 season and the lowest recorded temperature was -2.1°C in Lost Seal Stream in 2010/11.

All streams generally fluctuate between slightly acidic and slightly basic conditions. House Stream exhibited the largest variation with a pH range of 5.47 to 9.18 over the study period. The Onyx River was the most stable with a pH range of 6.20 to 8.44.

In general, all the streams showed similar ion concentrations. However, in Anderson Creek and House Stream the concentration of the calcium ion is higher than the chloride ion. In the Onyx River and Priscu Stream the opposite is true. In Lost Seal stream, the dominate ion fluctuates between calcium and chloride and often the concentrations of these two ions exhibit very similar values. The dominate cation in Dry Valley streams is calcium and bicarbonate is the dominant anion on an equivalent basis.

The concentration of each ion (mmol/L), in McMurdo Dry Valley streams and the corresponding stream field measurements, including temperature (°C), pH, and alkalinity (meq/L) can be found in the appendix.

4.2 Surface Sediment Analysis. Surface stream sediment was analyzed from all four Taylor Valley streams. Both SEM and XRD analyses were done on Anderson Creek, House Stream, and Lost Seal Stream sediments but only XRD analysis was completed on Priscu Stream surface sediments. In total, over 30 mineral phases were identified including common sedimentary, igneous, and metamorphic minerals (Table 1). SEM work revealed secondary weathering minerals products such as chlorite, clinochlore, smectite, vermiculite, and halloysite. Halloysite, a weathering product of feldspars in rocks like basalt or dolerite, is somewhat common in Taylor and Wright Valley and was identified by SEM analysis in Lost Seal and Priscu Stream. Volcanic ash, probably emanating from nearby Mount Erebus on Ross Island, was also present in all surface sediment samples. Common aluminosilicate minerals including many types of feldspar like albite, orthoclase, microline, oligoclase, labrdorite, and anorthite were observed (Table 1).

Table 1. XRD and SEM results.

Anderson Creek		**House Stream**	**Lost Seal**	**Priscu Stream**[†]
Allanite	Microcline	Albite, clacian	Albite, sodian	Albite, calcian
Albite, calcian	Muscovite	Amphibole	Albite, calcian	Amphibole
Aluminotaramite	Oligoclase	Anorhite, sodian	Amphibole	Anorthite
Apatite	Orthoclase	Augite	Augite	Augite
Barite	Phlogopite	Biotite	Chlorite[w]	Calcian
Biotite	Quartz	Calcite	Diopside, ferrous	Diopside, calcian
Calcite	Smectite[w]	Chlorite[w]	Halloysite[w]	Halloysite[w]
Chlorite[w]	Tremolite	Goethite	Illmenite	Orthoclase
Clinochlore[w]	Zircon	Hematite	Microcline	Quartz
Diopside		Labradorite	Microcline, sodian	
Epidote		Microcline, sodian	Orthoclase	
Fayalite		Orthoclase	Pyroxene	
Fosterite		Othoenstatite	Quartz	
Hornblende		Quartz	Smectite[w]	
Illmenite		Vermiculite[w]	Tremolite	

[w] denotes secondary weathering product
† XRD analysis only

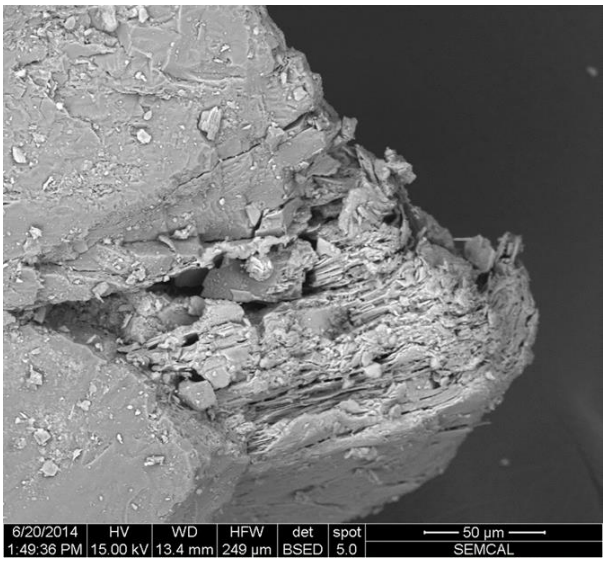

Figure 5. Dissolution of mica bounded by feldspar in Anderson Creek Sediment.

Figure 6. Volcanic ash found in Lost Seal sediment.

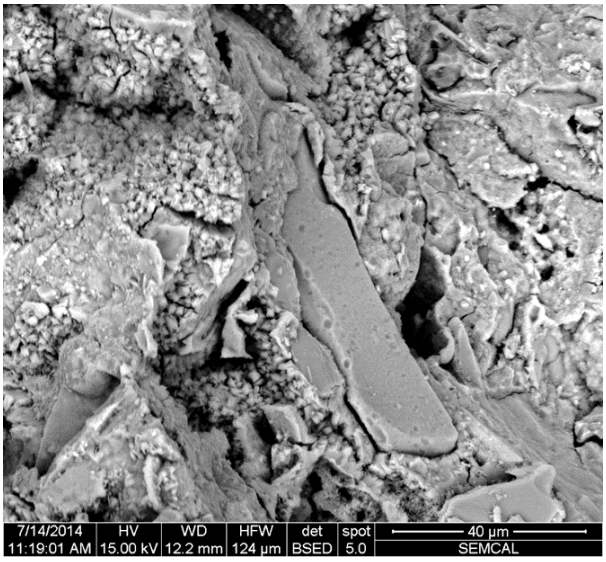

Figure 7. Etch pits, evidence of chemical weathering, visible on an apatite grain surrounded by smectite.

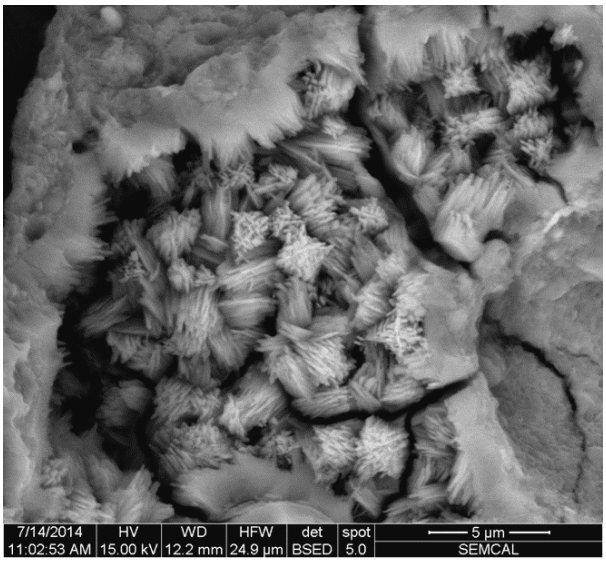

Figure 8. Smectite**,** a secondary weathering product, in Lost Seal sediment.

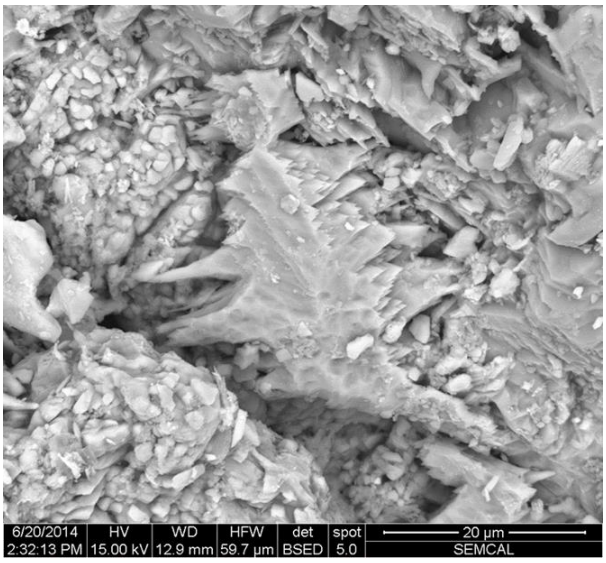

Figure 9. Chemical alteration of calcite producing a distinctive tooth-like pattern.

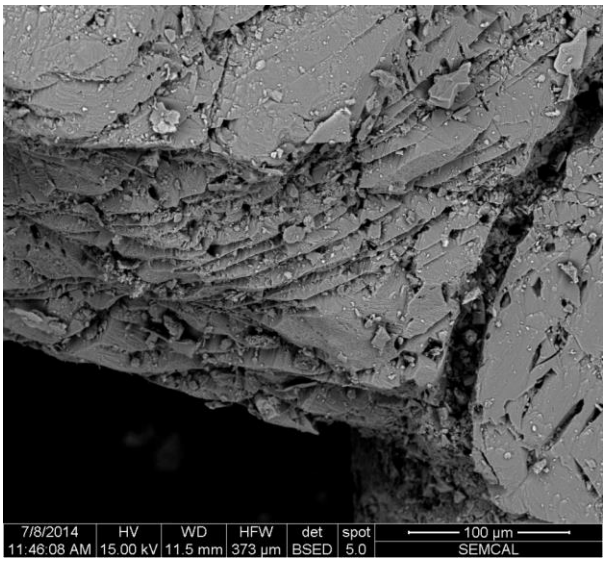

Figure 10. Dissolution of feldspar in House Stream sediment.

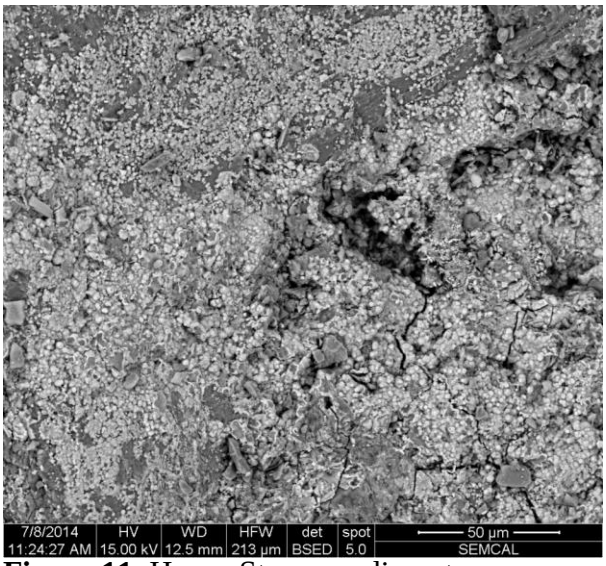

Figure 11. House Stream sediment.

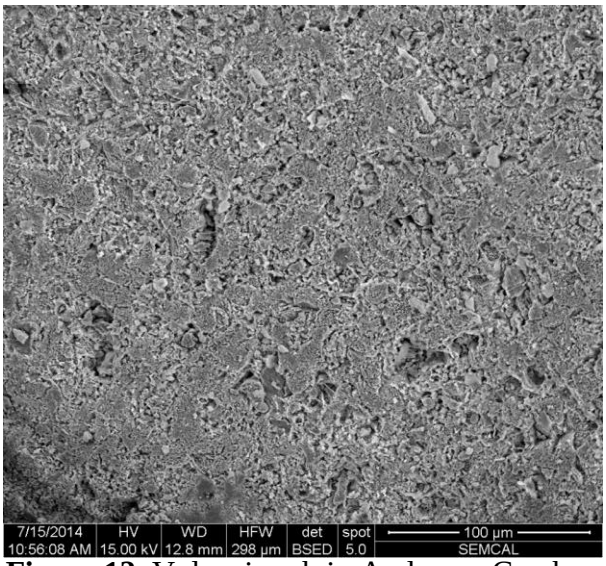

Figure 12. Volcanic ash in Anderson Creek sediment.

4.3 PHREEQ.

The mineral solubility modeling results suggest that all streams are undersaturated with respect to anorthite, calcite, albite, amorphous silica (SiO_2•nH_2O), dolomite, fluorite, and gypsum throughout the study period. Two mineral phases, kaolinite and k-mica, oscillate between undersaturated and supersaturated. Occasionally, calcite is close to saturation in some streams Albite became increasingly undersaturated as the temperature was progressively raised. Amorphous silica also showed a trend of becoming increasingly understaturated but at a much slower rate than albite. Calcite becomes less undersaturated as temperatures increases. Kaolinite exhibits the most noticeable effect of increased temperatures, and becomes undersaturated in House Stream above 5°C, and in Lost Seal Stream becomes undersaturaed 20°C. Anderson Creek remain supersaturated but approaches equilibrium at 20°C (Table 2).

Table 2. Saturation index of select minerals in Anderson Creek modeled over time. (Negative numbers represent samples that are undersaturated with respect to the listed mineral phase.)

Stream	Year	Anorthite	Calcite	Albite	Kaolinite	SiO_2 (a)	Dolomite	Fluorite	Gypsum	K-Mica
Anderson	1994/95	-18.29	-3.67	-9.93	-4.68	-1.27	-8.23	-3.79	-2.97	-7.94
	1995/96	-10.11	-2.83	-6.94	1.26	-1.79	-6.71	-3.68	-3.63	2.02
	1996/97	-5.74	-0.56	-3.20	2.47	-1.09	-2.05	-2.23	-2.19	5.59
	1998/99	-8.06	-2.08	-6.36	1.49	-1.90	-5.25	-2.08	-3.77	3.12
	2002/03	-9.53	-2.25	-6.05	1.51	-1.46	-5.56	-3.07	-3.01	2.59
	2004/05	-7.70	-3.01	-4.27	3.10	-1.22	-6.28	-3.55	-2.81	5.45
	2005/06	-12.63	-2.66	-6.99	-0.86	-1.28	-6.27	-2.79	-0.95	-1.24
	2006/07	-7.51	-1.63	-5.62	1.08	-1.71	-4.26	-3.63	-3.28	3.03
	2007/08	-7.12	-1.35	-5.21	1.00	-1.60	-3.63	-3.75	-2.69	3.10
	2008/09	-7.00	-2.25	-3.08	3.42	-1.15	-4.05	-3.55	-2.40	6.40
	2009/10	-6.79	-1.55	-4.74	2.71	-1.48	-4.23	-2.87	-2.75	5.07
	2010/11	-18.09	-3.40	-10.3	-4.91	-1.38	-7.89	-3.17	-2.95	-8.13

Table 3. Saturation index of select minerals in House Stream modeled over time.

Stream	Year	Anorthite	Calcite	Albite	Kaolinite	SiO_2 (a)	Dolomite	Fluorite	Gypsum	K-Mica
House	1994/95	-8.62	-0.06	-7.44	-1.55	-2.32	-2.46	-3.97	-3.46	-0.34
	1995/96	-8.86	-1.88	-8.11	1.23	-2.38	-5.31	-3.82	-3.7-	2.18
	1996/97	-9.87	-2.25	-7.84	1.01	-2.28	-5.77	-3.77	-3.42	1.54
	1998/99	-8.79	-2.07	-7.71	1.07	-2.35	-5.5	-	-3.77	2.06
	2002/03	-8.27	-2.00	-7.26	1.87	-2.07	-5.38	-4.07	-3.29	3.1
	2004/05	-9.02	-0.24	-8.2	-3.13	-2.49	-1.71	-	-3.5-	-2.32
	2005/06	-15.26	-3.45	-10.4	-2.09	-2.07	-8.15	-	-3.21	-4.3
	2006/07	-8.11	-1.07	-7.18	0.08	-2.12	-3.41	-4.02	-3.35	1.4
	2007/08	-8.01	-0.93	-6.65	0.18	-2.12	-3.12	-	-3.05	1.71
	2008/09	-7.49	-1.32	-5.42	2.18	-1.77	-3.56	-2.72	-2.07	4.05
	2009/10	-7.8	-0.99	-6.50	0.64	-2.02	-3.2	-3.01	-3.14	2.26
	2010/11	-18.58	-3.25	-12.0	-5.40	-2.04	-7.89	-3.51	-2.95	-9.15

Table 4. Saturation index of select minerals in Lost Seal Stream modeled over time.

Stream	Year	Anorthite	Calcite	Albite	Kaolinite	SiO_2 (a)	Dolomite	Fluorite	Gypsum	K-Mica
Lost Seal	1994/95	-8.67	-2.19	-4.89	1.57	-1.37	-4.85	-2.69	-3.50	3.00
	1995/96	-7.13	-1.99	-4.66	2.52	-1.43	-4.64	-3.69	-3.62	4.57
	1996/97	-6.60	-0.47	-3.82	0.55	-1.41	-1.52	-3.27	-3.15	3.10
	1998/99	-7.32	-2.06	-4.97	2.05	-1.49	-4.72	-3.74	-3.91	3.98
	2002/03	-11.52	-3.26	-6.91	0.32	-1.46	-7.22	-3.91	-3.90	0.28
	2004/05	-7.29	-1.70	-5.02	1.50	-1.54	-4.05	-3.94	-3.74	3.47
	2005/06	-7.54	-2.03	-3.81	2.68	-1.03	-4.62	-2.9	-2.76	4.64
	2006/07	-7..02	-1.28	-4.99	0.59	-1.49	-3.18	-3.58	-3.61	2.51
	2007/08	-6.27	0.11	-3.82	0.06	-1.23	-0.48	-3.18	-3.16	2.63
	2008/09	-6.14	-1.47	-3.22	3.48	-1.14	-3.55	-2.93	-2.07	5.62
	2009/10	-6.85	-0.04	-4.55	-1.27	-1.4	-0.77	-3.56	-3.56	0.76
	2010/11	-6.01	-0.99	-3.03	3.27	-1.17	-2.78	-2.62	-2.62	6.31

Table 5. Saturation index of select minerals in Priscu Stream modeled over time.

Stream	Year	Anorthite	Calcite	Albite	Kaolinite	SiO_2 (a)	Dolomite	Fluorite	Gypsum	K-Mica
Priscu	1994/95	-3.07	-1.32	-4.45	2.42	-1.43	-3.05	-2.94	-2.56	4.82
	1995/96	-7.44	-1.67	-5.34	2.39	-1.59	-4.11	-3.10	-2.93	4.38
	1996/97	-6.34	-0.06	-3.89	1.25	-1.29	-1.52	-2.73	-2.62	3.91
	1998/99	-10.11	-2.50	-5.78	1.05	-1.33	-5.25	-2.08	-3.77	3.12
	2002/03	-6.46	1.14	-4.25	1.58	-1.31	-5.56	-3.07	-3.01	2.59
	2004/05	-6.38	-1.0	-3.97	2.39	-1.32	-6.28	-3.55	-2.81	5.45
	2005/06	-12.15	-2.65	-7.09	-0.47	-1.4	-6.27	-2.79	-2.23	-1.24
	2006/07	-6.63	-1.28	-4.31	2.11	-1.37	-4.26	-3.63	-3.28	3.03
	2007/08	-6.28	-0.26	-3.7	0.83	-1.27	-3.63	-3.75	-2.69	3.10
	2008/09	-6.72	-1.59	-3.82	3.11	-1.24	-4.05	-3.55	-2.40	6.40
	2009/10	-6.36	-0.96	-4.00	1.82	-1.32	-4.23	-2.87	-2.75	5.07
	2010/11	-17.99	-3.19	-10.4	-5.36	-1.45	-7.89	-3.17	-2.95	-8.13

Table 6. Saturation index of select minerals in Onyx River modeled over time.

Stream	Year	Anorthite	Calcite	Albite	Kaolinite	SiO_2 (a)	Dolomite	Fluorite	Gypsum	K-Mica
Onyx	1994/95	-12.04	-3.30	-7.25	-0.57	-1.46	-5.72	-3.08	-3.90	-0.94
	1995/96	-12.54	-3.43	-7.54	-0.70	-1.46	-7.51	-3.36	-3.88	-1.29
	1996/97	-6.98	-2.01	-3.99	3.20	-1.26	-4.71	-2.84	-3.35	5.69
	1998/99	-7.06	-2.30	-4.39	2.72	-1.41	-5.28	-2.75	-3.43	5.07
	2002/03	-11.22	-3.20	-6.89	0.17	-1.46	-7.00	-3.49	-3.67	0.20
	2004/05	-7.71	-2.45	-4.84	2.73	-1.42	-5.60	-3.13	-3.49	4.69
	2005/06	-7.52	-2.84	-4.71	2.86	-1.41	-6.42	-3.25	-3.39	4.84
	2006/07	-6.80	-1.48	-4.22	1.77	-1.35	-3.64	-3.04	-3.4	4.16
	2007/08	-6.88	-1.23	-4.31	0.93	-1.34	-3.16	-3.51	-3.64	3.23
	2008/09	-7.34	-2.37	4.42	2.96	-1.34	-5.41	-3.07	-3.43	5.20
	2009/10	-7.19	-2.10	-4.82	2.05	-1.45	-4.90	-3.33	-3.78	4.13
	2010/11	-7.14	-1.21	-4.68	0.29	-1.44	-3.09	-3.54	-3.77	2.48

5. Discussion.

5.1 Surface Sediment Analysis. Both SEM and XRD analysis showed direct evidence of chemical weathering in all observed McMurdo Dry Valley ephemeral streams. Previous investigations have inferred that chemical weathering is an active geochemical process in these streams by observing that solute concentrations increase throughout the length of the stream and that stream geochemistry cannot be explained by salt dissolution alone, among other lines of evidence (Lyons et al., 1997; Lyons et al., 1998; Gooseff et al., 2002). Dissolution features were found on minerals in all Taylor Valley stream surface sediment during SEM analysis. Evidence of dissolution was identified qualitatively by the observation of morphological features commonly associated with chemical weathering. Figure 5 is an example of one such dissolution feature of mica. The edge of the mica shows evidence of chemical dissolution by the tattered and frayed edge sites (Maurice et al., 2002). These edge sites are thought to be more reactive than the basal-plane surfaces of mica. The observation of chemical weathering features in mica is consistent with Maurice et al. (2002) who concluded that aluminosilicate dissolution is occurring in the Dry Valleys. That study used an in-situ microcosm approach to observe the initial dissolution rate and features of basal-plane surface muscovite dissolution (shallow, anhedral etch pits) over a brief period of time (Maurice et al., 2002). Gooseff et al. (2002) speculated that biotite weathering accounted for the downstream increase in K^+ in Taylor Valley Streams. Maurice et al. (2002) did not provide direct evidence of other chemical weathering of other common aluminosilicate minerals found in the hyporheic zone of the streams nor observed any long-term dissolution features. Deep etch pits can be observed in other aluminosilicate minerals, such as the feldspar (Figure 10). Etch pits were also visible in phosphate minerals like apatite (Figure 7). Numerous, small etch pits can be observed on the face of the apatite grain and much larger etch pits are apparent on the grain edges.

Figure 9 is an example of chemical alteration of calcite in Anderson Creek surface sediment. The grain provides representation of the significant chemical alteration of minerals that is capable in Dry Valley streams. A saw-tooth geometry can be identified which is indicative of dissolution. The extensive formation of these sawtooth features, large etches pits, and apparent void space surrounding the grain may suggest that a large portion of the original grain has been dissolved over time. Combined with no evidence of a precipitated calcium carbonate, this may

indicate a stream geochemistry that is consistently undersaturated with respect to calcite. These results, however, cannot be extrapolated to other streams as each stream has a different chemistry. Carbonate minerals exist throughout the McMurdo Dry Valleys and are thought to have been produced in situ (i.e. pedogenic) as salt crusts and coatings or deposited during lake high stands as lacustrine $CaCO_3$ (Keys and Williams, 1981; Doran et al., 1994). The dissolution of these minerals is an important source of Ca^{2+} to the streams.

The observation of dissolution features on a variety of types of minerals suggests stream geochemistry is partially controlled by the composition of the sediment mineralogy that the water contacts during flow. For example, the Na^{+} increases in solution could result from the dissolution of salts or from the chemical weathering of aluminosilicate minerals like plagioclase. This thesis does not attempt to identify all the sources of the solutes, but it is also important to recognize the importance of ion exchange reactions in the hyporheic zone in these streams (Toner et al., 2013).

Clay minerals are layer silicates and among the most common products of chemical weathering. Their presence in all Taylor Valley stream surface sediments may indicate the significance of chemical weathering in these streams. Smectite is a clay derived from the chemical weathering of silicate minerals in alkaline conditions in igneous rocks (Figure 8). Volcanic ash is easily discernable from other grains by its vesicular texture and is commonly found in stream surface sediments (Figure 12). Often smectite is a secondary weathering product of volcanic ash. The occurrence of both volcanic ash and abundant smectite suggests that the chemical weathering of volcanic materials is readily occurring in the hyporheic zone channels and contributes ions such as Na^{+}, Mg^{2+}, K^{+}, and Ca^{2+} to the streams. Another clay mineral, halloysite, forms from the weathering of the glassy constituents finely divided volcanic ash (Claridge and Campbell, 1974). XRD analysis confirmed the presence of halloysite in both Lost Seal and Priscu Streams.

XRD and SEM results provide examples of indirect observation of primary aluminosilicate dissolution, and the possible formation of secondary weathering products (Figures 5,7,8,9,10) . These results also support the notion that primary aluminosilicate weathering is an important process in controlling stream geochemistry. Furthermore, the stream surface sediments may undergo significantly less chemical weathering than the sediment in the hyporheic zone due to

variation in flow rates and water: rock ratios. So, the extent of chemical weathering in hyporheic zone sediments may be much greater than the surface sediments.

5.2 PHREEQC. The PHREEQC results in this study corroborate the findings of Gooseff et al. (2002) who concluded that chemical denudation rates in McMurdo Dry Valley streams are significantly affected by stream discharge. The exchange of water with the sediment in the hyporheic zone removes weathering products from mineral surfaces and provides dilute meltwater that enhances chemical weathering. The saturation index of kaolinite in three Taylor Valley streams from 1994/95 to 2009/10 ranged from -4.68 to 3.5 (Figure 16). The saturation index of kaolinite in Anderson Creek, House Stream, and Lost Seal Stream during the 1994/95 was -4.68, -1.55, and -1.57, respectively. These negative saturation indices coincide with an extremely low flow year throughout the McMurdo Dry Valleys and the lowest flow year during this study. The low saturation states of kaolinite in each of these streams suggest that chemical weathering is significantly less in low flow years because kaolinite is a secondary weathering product and not being produced. The formation of kaolinite is dependent on the interaction between feldspar and water. The formula for the weathering of k-feldspar to kaolinite is represented by the equation:

$$(2)\ 4KAlSi_3O_8 + 4H^+ + 2H_2O \rightarrow 4K^+ + Al_4Si_4O_{10}(OH)_8 + 8SiO_2$$

The negative saturation index of kaolinite during the low flow season is lower than all other years, when stream discharge was higher. The same result is true of other minerals. For example, calcite has a saturation index of -3.67 in 1994/95 in Anderson Creek. The following field season it is -2.83 and by 1996/97 it is -0.56. Similar results are found of albite. The 1994/95 saturation index is -9.93 and by 1996/97 it is -3.20, a change of over 5 orders of magnitude in two years.

Kaolinite has a positive saturation index (i.e. deposition) in all three streams for 9 of the 12 observed field seasons. This is consistent with the SEM and XRD analysis which found the occurrence of secondary weathering products including chlorite, clinochlore, halloysite, Smectite, and vermiculite in stream sediments. The years of negative saturation indices correspond to low flow years and indicate that kaolinite was not supersaturated in those years. The absence of kaolinite may suggest that primary aluminosilicate minerals were not being chemically weathered to produce secondary weathering products due to a lack of hydrologic exchange in the hyporheic zone.

All three Taylor Valley streams are consistently undersaturated (between one and two orders of magnitude) with respect to amorphous silica (Figure 14). The relatively constant saturation indices, ranging from -2.49 to -1.03, in all three streams suggest that the chemical weathering of amorphous silica may be less dependent on stream discharge than the other minerals. Diatoms, photosynthetic algae that have an amorphous siliceous skeleton (frustule), are present in Dry Valley streams (KcKnight et al., 1999). The constant undersaturation of amorphous silica may result in the dissolution of these frustules over time. Changes to the saturation index of amorphous silica could have ecological impacts if stream geochemistry becomes more caustic to amorphous silica.

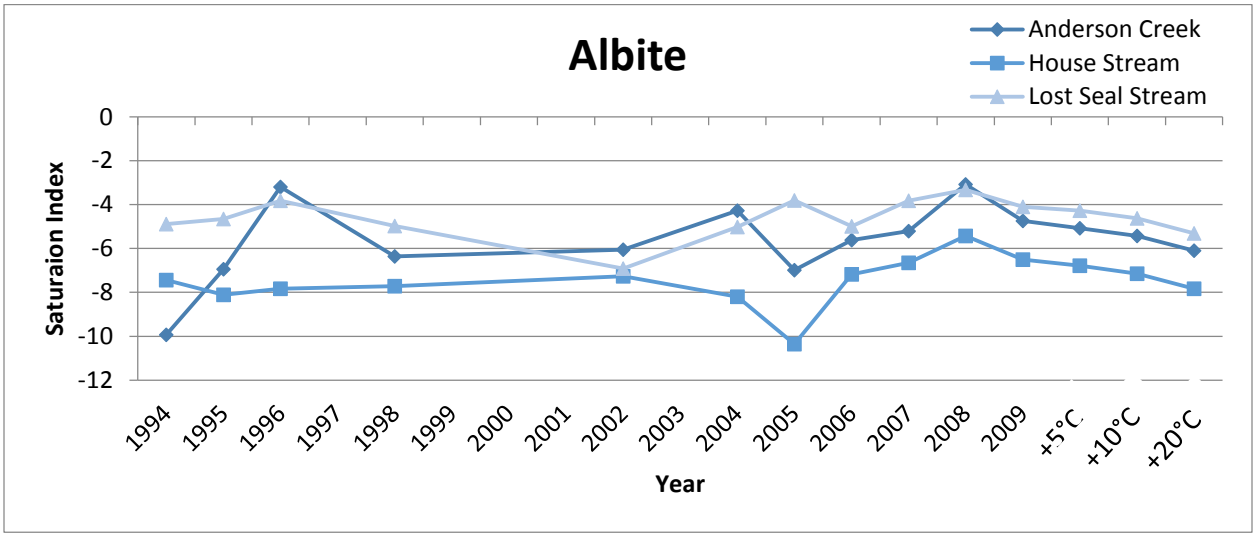

Figure 13. Albite saturation index over time in three Taylor Valley streams.

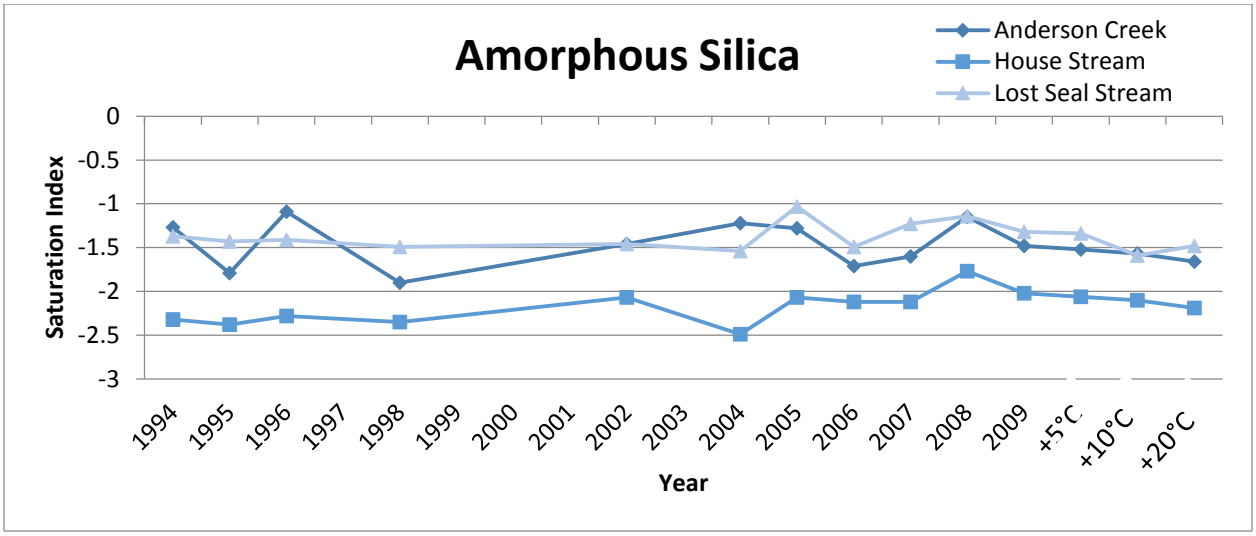

Figure 14. Amorphous silica saturation index over time in three Taylor Valley streams.

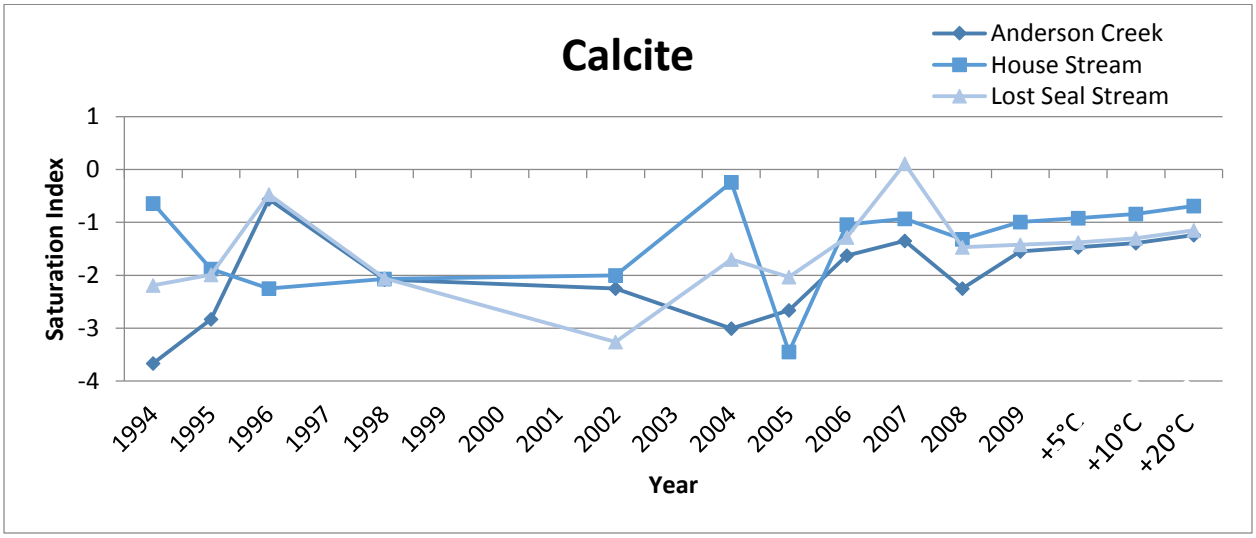

Figure 15. Calcite saturation index over time in three Taylor Valley streams.

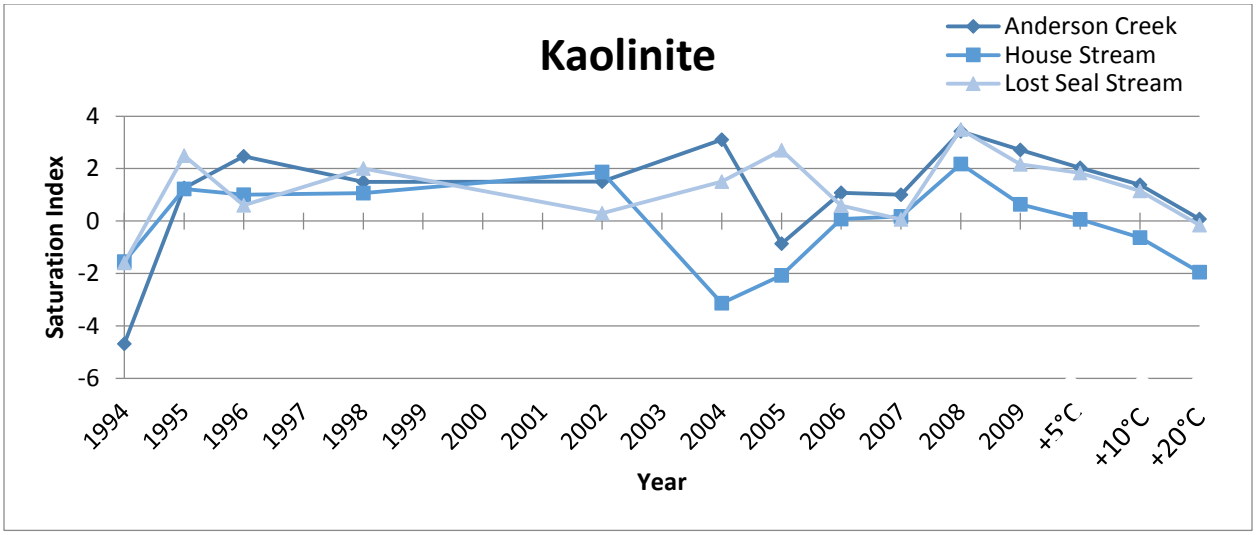

Figure 16. Kaolinite saturation index over time in three Taylor Valley streams.

Calcite and dolomite are continuously undersaturated in all Taylor Valley Streams. Based on Sr isotopic measurements Dowling et al., (2013) have argued that the dissolution of carbonate minerals is a major process in Taylor Valley streams. Calcite is typically between 1 and 4 orders of magnitude undersaturated (Figure 15). The PHREEQ results are consistent with the SEM findings which found evidence of dissolution features on calcium carbonate grains and no evidence of precipitation. Some streams occasionally approached equilibrium with respect to calcite, however, this was not observed for dolomite. Dolomite was consistently multiple orders of magnitude undersaturated than calcite and was never modeled to reach equilibrium or supersaturation.

SEM and XRD analysis confirmed the occurrence of many primary aluminosilicate minerals within the alluvium. The streams are undersaturated by about three to seven orders of magnitude with respect to these minerals, such as albite, the sodium endmember of plagioclase feldspar (Figure 13). Anorthite, the calcium endmember of plagioclase feldspar is also often several orders of magnitude more undersaturated than albite.

The PHREEQC simulations indicate that temperature is not a primary control on chemical weathering in Dry Valley Streams. This is different from results from temperate streams which indicate that temperature and precipitation are the primary factors (Nezat et al. 2001). While precipitation is not a large factor in the Dry Valley environment, PHREEQC models suggest the

presence, quantity, and hyporheic exchange of glacial meltwater controls chemical weathering in Dry Valley streams. The influence of increased water temperature in Dry Valley streams was negligible in calcite solubility in Anderson Creek, House Stream, and Lost Seal Stream. Calcite has a higher solubility in cold water so an increase of stream water temperature may cause the precipitation of calcite in stream margins. However, this study suggests even extreme increases of water temperature up to 20°C cannot explain the variability in the saturation index of calcite observed during the study period. For example, during the 1994/95 season, the saturation index of calcite in Anderson Creek was -3.67 and the water temperature was 1.2°C. Two years later the saturation index of calcite was -0.56 and the water temperature was 1.6°C (Figure 12). Figure 15 illustrates the lack of correlation between saturation index and water temperature. In 2009, the water temperature of Anderson Creek was 0.2°C and the saturation index of calcite was -1.55. The PHREEQC model suggest that raising the water temperature to 5°C, 10°C, and 20°C would raise the saturation index to -1.47, -1.39, and -1.24, respectively. A difference of 0.31 in the saturation index between the measured 2009 water temperature of 0.2°C and 20°C cannot explain the variability between field seasons as seen in 1994/95 and 1996/97. Increased temperatures also have a negligible effect on House Stream and Lost Seal Stream solubility results (Figure 15).

Similar findings can be seen in the solubility of amorphous silica (Figure 14). Anderson Creek had a saturation index of -1.48 using the measured 2009 water temperature of 0.2°C. Once again, the rise in water temperature cannot explain the variation of past saturation indices of amorphous silica. An increase of 5°C only decreased the saturation index 0.04 and an increase of 10°C decreased the saturation index by 0.09. Interestingly, in Lost Seal Stream the saturation index decreased when water temperatures were raised to 5°C and 10°C but rose when modeled under water temperature of 20°C. Amorphous silica has a relatively consistent saturation index over time, but the small deviations caused by increased temperature are still much smaller than deviations caused by the much smaller natural variations in water temperature.

Although significant changes in stream geochemistry are not predicted by water temperature alone, air temperature may be a significant control on long-term stream geochemistry by addition of increasing meltwater from glaciers. Future climate predictions indicate that Antarctic regions, including the McMurdo Dry Valleys, will gradually warm (Chapman and Walsh, 2007). This

will lead to increased glacial melt, and therefore higher stream discharge. Increased stream discharge will increase the volume of the hyporheic zone and perhaps its exchange dynamics as well and thus aid in increasing the chemical weathering rates of the sediments contained in them. Wide, flat channel streams, like Lost Seal Stream or Onyx River, may show higher variations in chemical weathering than incised channels because a much larger volume of the hyporheic zone is saturated during high stream flow compared to low flow (Nezat et al., 2001).

PHREEQC solubility results strongly support previous research that concluded stream discharge plays an important role in chemical weathering. Annual stream discharge in 2008 was much higher than previous years and one of the highest annual discharges on record (www.mcmlter.org). The increased interaction between the meltwater and hyporheic zone (i.e. chemical weathering) may have caused the increase of all ion concentrations observed in House Stream in 2008 (Table A2). These higher concentrations of major ions result in higher saturation indices of albite, amorphous silica, and kaolinite in Anderson, House, and Lost Seal streams (Figures 13-16).

6. Conclusions.

- SEM images revealed direct evidence of chemical weathering of aluminosilicate and carbonate minerals showed chemical dissolution features in stream surface sediments. Additionally, the occurrence of secondary minerals produced through chemical weathering in both SEM and XRD analysis supports the notion that chemical weathering is actively occuring in McMurdo Dry Valley streams.
- The minerals observed in XRD analysis is consistent with inferred results from SEM images and support the PHREEQC geochemical modeling solutions. Surface sediment mineralogy is consistent with the surrounding sedimentary, igneous, and metamorphic lithology. Volcanic ash from Mount Erebus is relatively common in McMurdo Dry Valley sediment and is found in all surface samples. Halloysite, a secondary weathering product, is likely derived from the volcanic ash.
- Streams are grossly undersaturated (from about three to seven orders of magnitude) with respect to albite. In most years, streams are between one and three orders of magnitude undersaturated with respect to calcite. Occasionally streams may approach equilibrium, with this phase, but supersaturation never occurs. Streams are typically supersaturated with respect to kaolinite leading to mineral precipitation. During low flow years kaolinite may become undersaturated. Streams are constantly undersaturated between one and two orders of magnitude with respect to amorphous silica.
- Changes in mineral saturation indices over time cannot be directly attributed to variations of stream water temperature. However, chemical weathering may be controlled indirectly through increased glacier meltwater production and hydrologic exchange in the hyporheic zone.
- Future increased air temperatures predicted in the McMurdo Dry Valley region will not raise stream water temperatures sufficiently to affect chemical weathering or stream geochemistry. An increase of air temperatures will cause more glacial melt that could greatly affect future stream geochemistry.

7. Recommendation for Future Work. Analysis of surface sediments and PHREEQC modeling for additional streams may provide a better understanding of the morphological and physical controls of chemical weathering inherent to Dry Valley streams. It would also be beneficial to examine stream sediment from different parts of the hyporheic zone. Sediment collected from the edges of the hyporheic zone or surface sediment may be significantly less altered from chemical weathering than sediment collected firmly within the hyporheic zone, which may give a better representation of the magnitude of the chemical weathering in ephemeral Dry Valley Streams. Additional geochemical modeling using PHREEQC and NETPATH could be used to develop a conceptual model by utilizing their reverse-modeling capabilities and available kinetic information to predict the impact of increased water flow due to glacier melt and increased temperatures.

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Appendix.

Table A1. Anderson Creek ion concentrations and field measurements.

Stream	Year	Temp.	pH	Alk.	Ca	Cl	K	Mg	Na	SO_4	Si	F
Anderson	1994/95	1.2	5.3	0.732	0.309	0.186	0.057	0.076	0.26	0.127	0.0634	0.00289
	1995/96	0.0	6.6	0.43	0.179	0.111	0.034	0.033	0.151	0.042	0.019	0.004
	1996/97	1.6	7.8	1.3	0.803	0.649	0.118	0.176	0.5	0.367	0.0983	0.01147
	1998/99	0.25	7.53	0.329	0.151	0.085	0.022	0.025	0.085	0.035	0.0147	0.027
	2002/03	0.2	6.6	0.819	0.383	0.179	0.053	0.066	0.194	0.092	0.0406	0.00574
	2004/05	1.7	6.86	0.21	0.14	0.5	0.081	0.141	0.33	0.415	0.0719	0.00579
	2005/06	0.1	6.17	0.63	0.572	0.516	0.077	0.128	0.421	0.433	0.0602	0.00684
	2006/07	1.2	7.91	0.303	0.191	0.125	0.03	0.037	0.128	0.091	0.0231	0.00421
	2007/08	2.9	7.95	0.32	0.317	0.265	0.04	0.064	0.189	0.236	0.031	0.00305
	2008/09	2.0	7.00	0.769	0.204	5.568	0.182	1.039	1.873	1.154	0.086	0.00574
	2009/10	0.2	7.335	0.654	0.447	0.25	0.046	0.066	0.198	0.15	0.0388	0.00674
	2010/11	2.0	5.42	0.774	0.399	0.188	0.061	0.06	0.157	0.103	0.0506	0.00526

Table A2. House Stream ion concentrations and field measurements.

Stream	Year	Temp.	pH	Alk.	Ca	Cl	K	Mg	Na	SO_4	Si	F
House	1994/95	0.0	8.70	0.437	0.227	0.129	0.019	0.031	0.113	0.05	0.0057	0.00253
	1995/96	0.3	7.10	0.687	0.32	0.059	0.017	0.018	0.05	0.021	0.0049	0.00258
	1996/97	0.1	6.70	0.69	0.354	0.244	0.021	0.038	0.197	0.038	0.0061	0.00263
	1998/99	0.5	7.27	0.406	0.231	0.112	0.015	0.019	0.09	0.024	0.0052	-
	2002/03	1.0	6.95	0.5	0.472	0.094	0.021	0.037	0.056	0.039	0.0101	0.00163
	2004/05	2.2	9.18	0.39	0.212	0.108	0.014	0.022	0.079	0.05	0.0043	-
	2005/06	0.5	5.55	0.66	0.323	0.159	0.019	0.035	0.113	0.066	0.01	-
	2006/07	2.2	7.94	0.645	0.324	0.082	0.02	0.027	0.066	0.048	0.0093	0.00211
	2007/08	0.5	8.00	0.65	0.399	0.226	0.027	0.042	0.184	0.08	0.009	-
	2008/09	2.0	7.00	1.137	1.015	1.068	0.058	0.221	0.602	0.396	0.0206	0.00595
	2009/10	1.00	7.83	0.769	0.419	0.173	0.028	0.049	0.141	0.063	0.0114	0.00595
	2010/11	0.38	5.47	0.867	0.482	0.157	0.03	0.042	0.11	0.087	0.0107	0.00316

Table A3. Lost Seal ion concentrations and field measurements.

Stream	Year	Temp.	pH	Alkalinity	Ca	Cl	K	Mg	Na	SO_4	Si	F
Lost Seal	1994/95	8.3	6.70	1.087	0.196	0.441	0.064	0.088	0.996	0.063	0.0595	0.01469
	1995/96	5.8	7.10	0.65	0.217	0.222	0.038	0.07	0.334	0.039	0.0486	0.00405
	1996/97	3.9	8.30	0.74	0.477	0.668	0.082	0.21	1.409	0.063	0.0495	0.00485
	1998/99	7.75	7.19	0.54	0.162	0.171	0.037	0.056	0.276	0.026	0.0441	0.00453
	2002/03	3.2	6.23	0.416	0.142	0.142	0.032	0.049	0.219	0.029	0.0428	0.00368
	2004/05	6.5	7.53	0.54	0.179	0.209	0.037	0.059	0.281	0.035	0.0385	0.00337
	2005/06	7.7	6.75	1.49	0.204	1.485	0.055	0.077	0.656	0.371	0.1282	0.01169
	2006/07	9.2	7.88	0.558	0.186	0.182	0.038	0.058	0.281	0.047	0.0456	0.00526
	2007/08	4.9	8.66	1.24	0.456	0.406	0.061	0.145	0.456	0.063	0.0775	0.00521
	2008/09	2.0	7.00	0.74	1.166	3.597	0.024	0.521	0.983	0.393	0.0868	0.00458
	2009/10	7.65	9.00	0.628	0.264	0.267	0.034	0.073	0.345	0.039	0.0587	0.00447
	2010/11	-2.1	7.54	1.357	0.579	0.725	0.082	0.209	0.9	0.175	0.0755	0.0079

Table A4. Onyx River ion concentrations and field measurements.

Stream	Year	Temp.	pH	Alkalinity	Ca	Cl	K	Mg	Na	SO_4	Si	F
Onyx	1994/95	5.9	6.30	0.35	0.14	0.199	0.033	1.63	0.22	0.044	0.0459	0.01174
	1995/96	4.3	6.20	0.322	0.126	0.159	0.03	0.046	0.17	0.034	0.0442	0.00742
	1996/97	0.5	7.10	0.67	0.25	0.336	0.006	0.1	0.379	0.064	0.0641	0.00921
	1998/99	1.5	7.30	0.264	0.19	0.315	0.46	0.076	0.323	0.066	0.047	0.01174
	2002/03	6.5	6.27	0.376	0.146	0.194	0.035	0.054	0.214	0.05	0.0464	0.00626
	2004/05	1.9	6.96	0.43	0.178	0.259	0.04	0.065	0.263	0.061	0.0456	0.0079
	2005/06	2.0	7.00	0.17	0.164	0.26	0.032	0.056	0.258	0.082	0.0474	0.00716
	2006/07	2.1	7.87	0.458	0.195	0.287	0.04	0.074	0.293	0.07	0.0545	0.00842
	2007/08	2.2	8.30	0.39	0.147	0.213	0.031	0.054	0.215	0.052	0.0566	0.00558
	2008/09	2.0	7.00	0.417	0.205	0.309	0.054	0.079	0.33	0.063	0.0559	0.00795
	2009/10	4.5	7.47	0.338	0.137	0.167	0.032	0.045	0.189	0.04	0.0459	0.00742
	2010/11	3.5	8.44	0.311	0.132	0.182	0.035	0.048	0.214	0.042	0.0463	0.00579

Table A5. Priscu Stream ion concentrations and field measurements.

Stream	Year	Temp.	pH	Alkalinity	Ca	Cl	K	Mg	Na	SO_4	Si	F
Priscu	1994/95	6.4	7.10	1.173	0.626	1.125	0.095	0.359	0.6	0.205	0.0495	0.00632
	1995/96	4.5	6.90	0.996	0.527	0.355	0.066	0.143	0.281	0.091	0.033	0.00526
	1996/97	8.3	7.80	1.23	0.604	1.213	0.125	0.376	0.796	0.189	0.0723	0.00853
	1998/99	1.0	6.56	0.651	0.289	0.46	0.061	0.17	0.366	0.078	0.0553	0.00879
	2002/03	11.2	7.43	0.763	0.55	0.988	0.111	0.264	0.554	0.12	0.0729	0.00979
	2004/05	2.6	7.53	1.16	0.55	0.81	0.05	0.254	0.489	0.131	0.0584	0.0079
	2005/06	1.58	6.27	0.9	0.277	0.298	0.044	0.103	0.267	0.066	0.0477	0.00747
	2006/07	3.7	7.56	0.764	0.37	0.542	0.068	0.186	0.338	0.079	0.0538	0.0079
	2007/08	1.9	8.43	0.97	0.484	0.994	0.089	0.281	0.555	0.124	0.0663	0.00832
	2008/09	2.00	7.00	0.895	0.666	1.39	0.108	0.347	0.706	0.161	0.0699	0.00842
	2009/10	8.00	7.48	0.922	0.741	1.362	0.127	0.373	0.818	0.253	0.0655	0.01347
	2010/11	6.60	5.42	0.958	0.454	0.372	0.061	0.146	0.282	0.078	0.0477	0.00895

Table A6. Saturation index for select Anderson Creek mineral phases.

Stream	Year	Calcite	SiO_2 (a)	Kaolinite	Albite
Anderson	1994/95	-3.67	-1.27	-4.68	-9.93
	1995/96	-2.83	-1.79	1.26	-6.94
	1996/97	-0.56	-1.09	2.47	-3.20
	1998/99	-2.08	-1.90	1.49	-6.36
	2002/03	-2.25	-1.46	1.51	-6.05
	2004/05	-3.01	-1.22	3.10	-4.27
	2005/06	-2.66	-1.28	-0.86	-6.99
	2006/07	-1.63	-1.71	1.08	-5.62
	2007/08	-1.35	-1.60	1.00	-5.21
	2008/09	-2.25	-1.15	3.42	-3.08
	2009/10	-1.55	-1.48	2.71	-4.74
	2009/10 (5°C)	-1.47	-1.52	2.03	-5.08
	2009/10 (10°C)	-1.39	-1.57	1.38	-5.43
	2009/10 (20°C)	-1.24	-1.66	0.08	-6.10

Table A7. Saturation index for select House Stream mineral phases.

Stream	Year	Calcite	SiO_2 (a)	Kaolinite	Albite
House	1994/95	-0.64	-2.32	-1.55	-7.44
	1995/96	-1.88	-2.38	1.23	-8.11
	1996/97	-2.25	-2.28	1.01	-7.84
	1998/99	-2.07	-2.35	1.07	-7.71
	2002/03	-2.00	-2.07	1.87	-7.26
	2004/05	-0.24	-2.49	-3.13	-8.20
	2005/06	-3.45	-2.07	-2.07	-10.35
	2006/07	-1.04	-2.12	0.08	-7.18
	2007/08	-0.93	-2.12	0.18	-6.65
	2008/09	-1.32	-1.77	2.18	-5.42
	2009/10	-0.99	-2.02	0.64	-6.50
	2009/10 (5°C)	-0.92	-2.06	0.06	-6.79
	2009/10 (10°C)	-0.84	-2.10	-0.63	-7.15
	2009/10(20°C)	-0.69	-2.19	-1.95	-7.84

Table A8. Saturation index for select Lost Seal mineral phases.

Stream	Year	Calcite	SiO_2 (a)	Kaolinite	Albite
Lost Seal	1994/95	-2.19	-1.37	-1.60	-4.89
	1995/96	-1.99	-1.43	2.50	-4.66
	1996/97	-0.47	-1.41	0.60	-3.82
	1998/99	-2.06	-1.49	2.00	-4.97
	2002/03	-3.26	-1.46	0.30	-6.91
	2004/05	-1.70	-1.54	1.50	-5.02
	2005/06	-2.03	-1.03	2.70	-3.81
	2006/07	-1.28	-1.49	0.59	-4.99
	2007/08	0.11	-1.23	0.06	-3.82
	2008/09	-1.47	-1.14	3.50	-3.32
	2009/10	-1.42	-1.32	2.17	-4.10
	2009/10 (5°C)	-1.38	-1.34	1.84	-4.27
	2009/10 (10°C)	-1.30	-1.59	1.15	-4.63
	2009/10 (20°C)	-1.15	-1.48	-0.16	-5.31